LABORATORY AND ASTRONOMICAL MEASUREMENT OF THE MILLIMETER WAVE SPECTRUM OF THE ETHYNYL RADICAL CCH

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ABSTRACT

The $N = 0 \to 1$ and $1 \to 2$ rotational transitions of CCH at 87 and 174 GHz, respectively, have been detected in a laboratory glow discharge in a mixture of He and C_2H_2. The spectroscopic constants of CCH derived from measurements of the hfs of these transitions are in excellent agreement with those derived from astronomical observations, conclusively confirming the astronomical detection of CCH (Tucker, Kutner, and Thaddeus). As the CCH lines in the Orion Nebula are even narrower than our laboratory lines but less certain in rest frequency owing to uncertainty in the radial velocity, the most accurate values for the spectroscopic constants of CCH are obtained from a simultaneous fit of both the laboratory and astronomical data: for the rotation, centrifugal distortion, spin-rotation, and hyperfine constants, respectively, we find $B_0 = 43674.534 \pm 0.006$ MHz, $D_0 = 0.1071 \pm 0.0008$ MHz, $\gamma = -62.606 \pm 0.004$ MHz, $b = 40.426 \pm 0.019$ MHz, and $c = 12.254 \pm 0.026$ MHz.

Subject headings: interstellar: molecules — laboratory spectra — molecular processes — radio sources: lines

I. INTRODUCTION

The CN radical has been studied for many years in the laboratory and in comets, the Sun, interstellar gas, and cool stellar atmospheres, but the isoelectronic ethynyl radical CCH has been extremely elusive. Despite many years of search, the CCH analogs of the familiar violet and red systems of CN have not been found by laboratory spectroscopists, although CCH trapped in inert gas matrices has been detected by electron spin resonance, (Cochran, Adrian, and Bowers 1964; Graham, Dismuke, and Weltner 1974). The first evidence for free CCH was interstellar: detection of six millimeter-wave lines near the expected frequency of the fundamental rotational transition, matching the hyperfine structure calculated from the ESR data (Tucker, Kutner, and Thaddeus 1974; Tucker and Kutner 1978). Evenson *et al.* (1980) subsequently detected free CCH by far–IR laser magnetic resonance in a methane-fluorine flame but, owing to the complexity of the molecular Zeeman effect, were unable to obtain precise enough values for the rotation and hyperfine constants of CCH to much increase confidence in the astronomical identification.

Here we report direct laboratory measurement of the two lowest rotational transitions of CCH in a helium-acetylene discharge, conclusively confirming the astronomical detection of this radical and yielding better values of its microwave constants. Saystry *et al.* (1981), following a different method of production, have also recently detected the rotational spectrum of CCH in the laboratory.

Included in our determination of the CCH microwave constants are very precise relative frequencies derived from previously unpublished astronomical observations of the hyperfine components of the $N = 1 \to 0$ rotational transition; the hyperfine splittings are more precisely determined from the astronomical spectra because of the higher signal-to-noise ratio and smaller line widths. Analysis of the combined laboratory and astronomical data reported here yields the most accurate values for the CCH microwave constants.

II. LABORATORY MEASUREMENTS

a) Apparatus

The free space millimeter wave absorption spectrometer with which we have detected CCH, C_3N, C_4H, and other reactive molecules is shown schematically in Figure 1. Ions and radicals are produced by a DC glow discharge between a cylindrical copper anode and a stainless steel cathode in a glass tube 2 m long by 15 cm in diameter. For CCH, signal power at the fundamental rotational transition at 87 GHz was supplied by an *R* band klystron phase-locked to a high harmonic of a frequency synthesizer, and at the second rotational transition at 174 GHz by the klystron's first harmonic from an efficient (15%–20%) frequency multiplier. The detec-
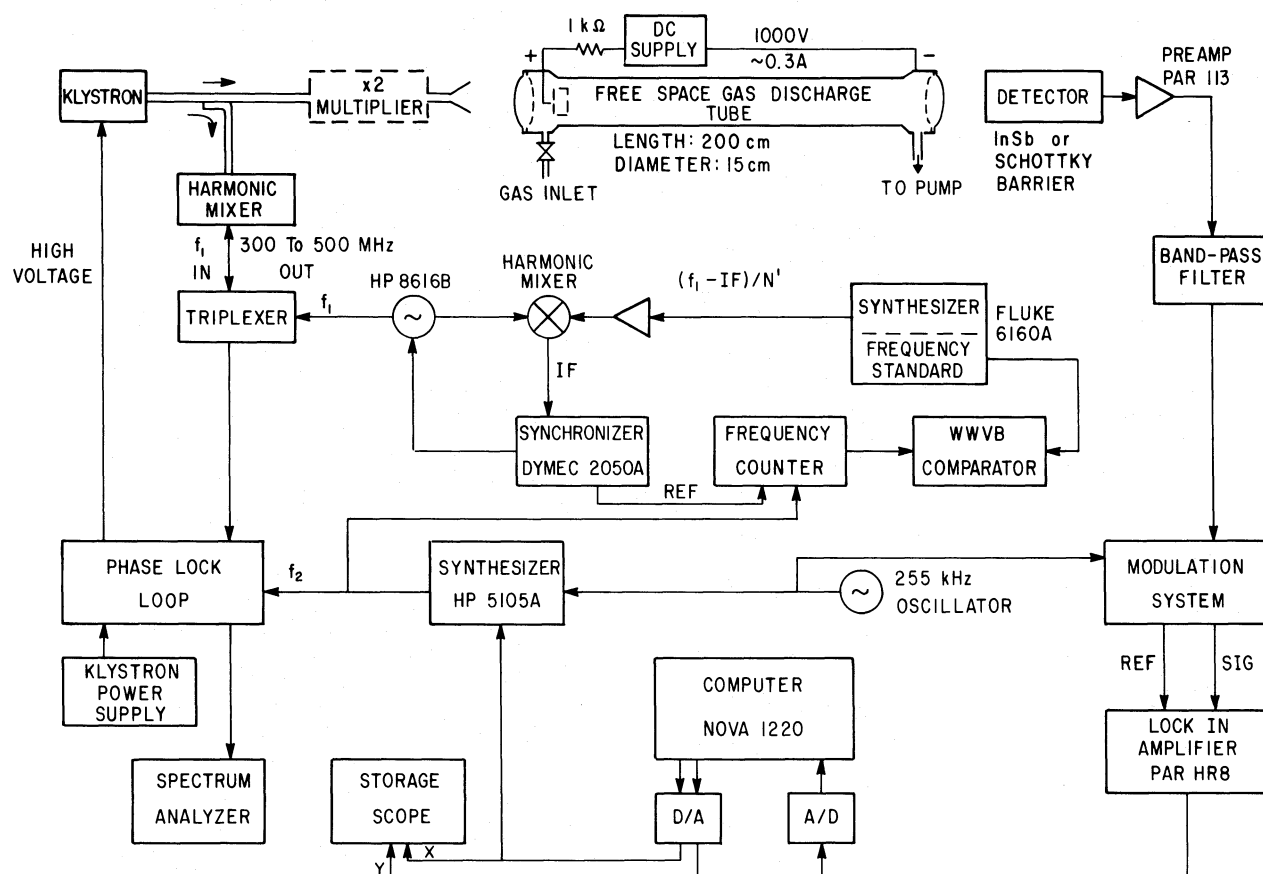
FIG. 1.—Block diagram of the millimeter-wave spectrometer

tor at 87 GHz was a room temperature Schottky barrier diode, and at 174 GHz a liquid He–cooled InSb hot electron bolometer (without magnetic field bias).

For both transitions, klystron modulation and second harmonic detection were used to reduce baseline distortion and noise. To suppress $1/f$ noise it is desirable to modulate at the highest frequency possible; a modulation frequency of 255 kHz was chosen because the sensitivity of the InSb bolometer decreases at higher frequencies. Modulation was applied via the phase-lock-loop reference oscillator (an HP 5105A frequency synthesizer) by means of the scheme described by Nagourney (1978), the klystron remaining locked because the modulation frequency is less than the bandwidth of the phase-lock circuit. For pressure-broadened absorption lines, the line shape is approximately the second derivative of a Lorentzian. The minimum detectable absorption coefficient of the spectrometer with a time constant of 30 s is $\sim 1 \times 10^{-8}$ cm^{-1}.

The phase-lock circuit used to stabilize the klystron is essentially that described by Weinreb (1970). An oscillator (HP 8616B) with frequency f_1 in the range 3.6 to 3.9 GHz was phase-locked to a harmonic of a Fluke 6160A frequency synthesizer by a commercial phase-lock circuit (Dymec 2050A); this signal at f_1 was then combined with the klystron signal in a harmonic mixer to produce an IF signal in the range 300 to 500 MHz. The klystron was swept by passing a ramp generated by the computer through the D/A convertor and applying it to the HP frequency synthesizer search oscillator.

At the start of a scan the frequency of the HP synthesizer was measured on the counter at 11 equally spaced points, the frequency of the internal reference to the Dymec synchronizer (labeled REF in Fig. 1) was measured, and the frequency of the Fluke synthesizer was recorded, the frequency at intermediate points in the spectrum then being obtained by linear interpolation. Drift of the HP synthesizer owing to the analog control of the search oscillator amounted to only a few 100 Hz in 10 minutes.

As a frequency check, measurements were made of O^{13}CS at 84,865 MHz, HCN at 88,633 MHz and 177,263 MHz, H$_2$S at 168,762 MHz, and OCS at 170,267 MHz; agreement with previous measurements (Lovas 1978) was always better than 14 kHz. To investigate the effect of a discharge on observed frequencies, the two HCN

transitions were, in addition, observed with the discharge on and off; no shift larger than 4 kHz was observed.

b) CCH Production

The CCH was generated in a DC glow discharge of an approximately equal molar mixture of He and C_2H_2 at a total pressure of 30 mTorr. To reduce the line width and the rotational partition function, the glass absorption cell was cooled by flowing liquid nitrogen through rubber tubing wound around the outside; the line widths (FWHM) were typically 1000 kHz. At a gas flow through the cell of ~ 1 liter s^{-1}, a stable discharge was obtained at currents of 0.3–0.4 A. When the discharge was run for several days, the copper anode suffered serious deterioration, and the millimeter wave transmission decreased by 10 to 15 dB because of a lossy deposit that formed on the inner surfaces of the teflon lenses, particularly that near the cathode.

The Matheson purified grade acetylene used in the experiment was slightly contaminated with acetone. There are strong acetone lines in the vicinity of the three strongest $N = 0 \rightarrow 1$ CCH transitions, but these could not be detected when the discharge was running and the absorption cell was cold—the conditions under which CCH was observed.

By comparing the signal-to-noise ratio of the CCH transition at 174,663 MHz with that of $^{18}OC^{34}S$ at 177,901 MHz, it is estimated that the CCH concentration is $\sim 4 \times 10^{10}$ cm^{-3} for an assumed dipole moment of 0.8 debyes (see Tucker, Kutner, and Thaddeus 1974) and a kinetic temperature of 100 K. An ion-molecule reaction is probably not responsible for the CCH produced in the He and C_2H_2 discharge, since the CCH concentration is approximately 10 times greater than HCO$^+$ observed under similar discharge conditions.

c) CCH Measurements

The three strongest CCH $N = 1 \rightarrow 2$ lines shown in Figure 2 were measured at 128 points equally spaced over ~ 4 MHz; the weakest line was measured at 68 points, and the three strongest $N = 0 \rightarrow 1$ lines were measured at 64 points. Although the CCH absorption profiles were observed on individual scans with an integration time of ~ 6 min, the signal-to-noise ratio was poor for the weaker transitions. Therefore, for each transition 10 scans were recorded with the direction of the frequency sweep reversed in successive scans.

A function describing a Lorenztian shaped signal detected at the second harmonic (Nagourney 1978) and a linear or quadratic baseline were simultaneously least-squares fitted to the data. Three free parameters characterizing the Lorentzian profile (frequency, line width, and intensity) and the baseline parameters were varied in the least-squares fit. For the strongest $N = 0 \rightarrow 1$ and the three strongest $N = 1 \rightarrow 2$ transitions the frequencies
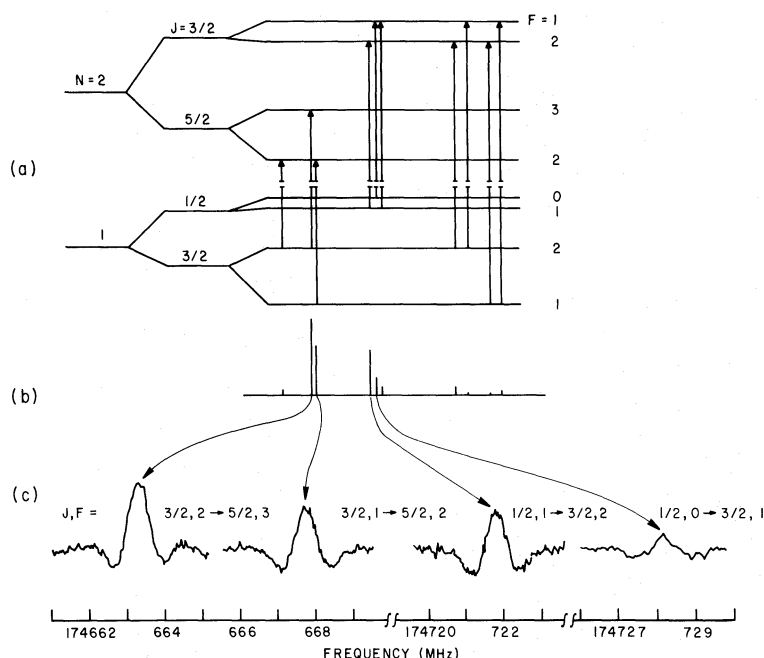

FIG. 2.—Laboratory spectrum of the $N = 1 \rightarrow 2$ transition of CCH. (a) The two rotational levels of the transition, split first by spin doubling, then by hfs (magnified $\times 3$); (b) the theoretical intensity ratios; (c) the laboratory lines adjusted in intensity to match the theoretical ratios. The total integration time for each line was ~ 60 minutes.

TABLE 1

LABORATORY CCH FREQUENCIES

$N \to N'$	$J \to J'$	$F \to F'$	Measured Frequencies[a] (MHz)	Measured-Calculated[b] (MHz)
$0 \to 1$.......	$1/2 \to 3/2$	$\begin{cases} 1 \to 2 \\ 0 \to 1 \end{cases}$	87316.924 ± 0.010 87328.623 ± 0.016	-0.004 $+0.006$
	$1/2 \to 1/2$	$1 \to 1$	87402.037 ± 0.040	$+0.030$
$1 \to 2$	$3/2 \to 5/2$	$\begin{cases} 2 \to 3 \\ 1 \to 2 \end{cases}$	$174,663.222 \pm 0.008$ $174,667.685 \pm 0.017$	-0.009 $+0.018$
	$1/2 \to 3/2$	$\begin{cases} 1 \to 2 \\ 0 \to 1 \end{cases}$	$174,721.777 \pm 0.026$ $174,728.100 \pm 0.040$	$+0.026$ $+0.046$

[a] Uncertainties are 1 σ as discussed in § IIc.
[b] From a least-squares fit to the combined laboratory and astronomical data.

in Table 1 are the mean values of 10 spectra that were analyzed separately, the quoted uncertainties representing the standard deviations of the mean. The frequencies of the three weakest transitions in Table 1 are the mean values of the frequencies derived from the average of scans measured in the positive and negative sweep directions, and the uncertainties are the standard errors of the mean based on the 1 σ standard deviations computed by the least-squares fitting program.

III. ASTRONOMICAL OBSERVATIONS

In 1975 November all six hyperfine components of the CCH fundamental rotational transition ($N = 1 \to 0$) were observed with the National Radio Astronomy Observatory[1] 36 foot (11 m) telescope 3′ N of the Kleinmann-Low Nebula in Orion, where the lines of CCH are particularly sharp and intense. The spectra (Fig. 3) were observed with a higher signal-to-noise ratio and better frequency resolution (100 kHz) than previously reported. The astronomical data are summarized in Table 2.

Although the uncertainties in the relative frequencies of the four strongest lines are less than 10 kHz, the uncertainties in the absolute frequencies are considerably larger owing to uncertainty in the CCH radial velocity. From observations of CN, HCN, HCO⁺ (Turner and Thaddeus 1977), and NH_3 (Ho et al. 1979) at the same position, the uncertainty in velocity is estimated to be 0.2 km s⁻¹, for an uncertainty in the absolute CCH frequencies in Table 2 of 60 kHz, and an uncertainty in the rotational constant of 30 kHz.

IV. ANALYSIS

The Hamiltonian that describes the rotation, spin-rotation, and magnetic hyperfine interactions in the

CCH $^2\Sigma$ ground state is (see Townes and Schawlow 1955)

$$\mathcal{H} = [B - N(N+1)D]N(N+1)$$
$$+ \gamma N \cdot S + bI \cdot S + cI_z S_z, \qquad (1)$$

where N is the total angular momentum excluding spin, and S and I are the electron and proton spin with components S_z and I_z along the (moving) molecular axis. Since the spin-rotation coupling constant is somewhat larger than the hyperfine constants b and c, the appropriate coupling scheme is

$$N + S = J, \qquad J + I = F. \qquad (2)$$

Matrix elements of the Hamiltonian off-diagonal in J are not negligible for the lower rotational transitions of CCH and must be retained in the computation of frequencies and intensities.

Five parameters (B, D, γ, b, and c) were least-squares fitted to the laboratory frequencies in Table 1, and these plus the Doppler velocity in the local standard of rest (V_{LSR}) were simultaneously fitted to both the laboratory and astronomical data. The uncertainties in γ, b, and c determined from the fit to the combined data are 10 times smaller than those determined from the laboratory data alone (see Table 3). The values for b and c are in excellent agreement, but γ differs by more than 1 σ. The values for γ, b, and c determined from the combined data are preferred because the transitions measured in the laboratory are less sensitive to the hyperfine constants, and the relative frequencies derived from the astronomical observations are very precise. The frequencies calculated using the parameters in Table 3 agree with the measured frequencies to within 1 σ, and the astronomical and laboratory $N = 0 \to 1$ frequencies are in satisfactory agreement. The V_{LSR} of 9.527 ± 0.031 km s⁻¹ derived for CCH from the fit to the combined
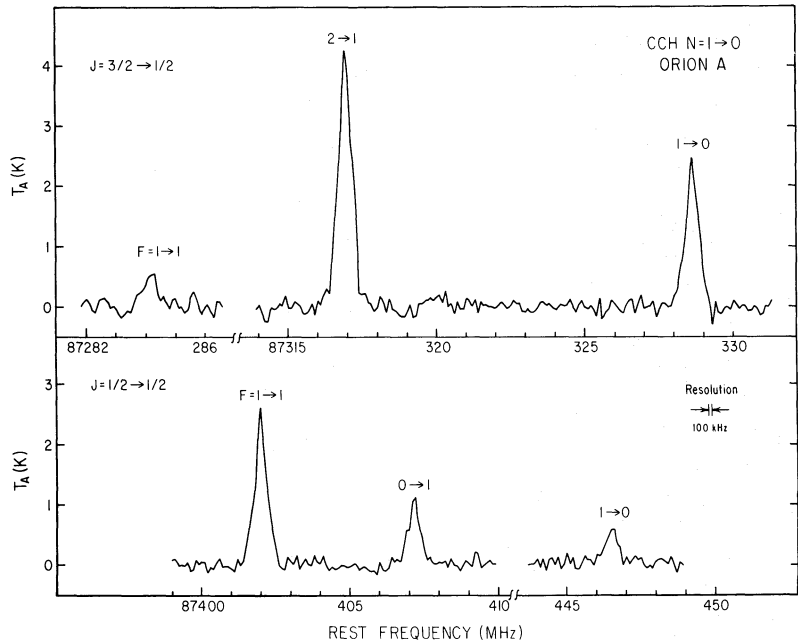
Fig. 3.—Astronomical $N = 1 \rightarrow 0$ CCH spectra observed 3' N of the Kleinmann-Low Nebula in Orion A at a frequency resolution of 100 kHz. The frequency scale is based on a Doppler velocity of 9.53 km s^{-1}.

TABLE 2

ASTRONOMICAL OBSERVATIONS OF THE CCH $N = 1 \rightarrow 0$ TRANSITION[a]

$J \rightarrow J'$	$F \rightarrow F'$	Rest Frequency[b] (MHz)	Measured-Calculated (MHz)	T_A (K)	$\Delta \nu$[c] (MHz)
$3/2 \rightarrow 1/2$ ...	$1 \rightarrow 1$	87284.156 ± 0.030	$+0.050$	0.530 ± 0.056	0.58 ± 0.07
	$2 \rightarrow 1$	87316.925 ± 0.004	-0.003	3.998 ± 0.065	0.53 ± 0.01
	$1 \rightarrow 0$	87328.624 ± 0.006	$+0.007$	2.272 ± 0.050	0.53 ± 0.01
$1/2 \rightarrow 1/2$ ...	$1 \rightarrow 1$	87402.004 ± 0.005	-0.003	2.254 ± 0.044	0.53 ± 0.01
	$0 \rightarrow 1$	87407.165 ± 0.011	$+0.005$	1.022 ± 0.050	0.49 ± 0.03
	$1 \rightarrow 0$	87446.512 ± 0.023	-0.006	0.560 ± 0.048	0.55 ± 0.05

[a]At a position 3' N of the Kleinmann-Low Nebula in Orion: $\alpha(1950) = 05^h32^m47^s$, $\delta(1950) = -05°21'21''$. Uncertainties are 1 σ, as determined by a least-squares fit of a linear baseline and Gaussian line profiles.
[b]For a Doppler velocity in the local standard of rest of 9.527 km s^{-1}, as determined from a simultaneous least-squares fit of the laboratory and astronomical data.
[c]FWHM uncorrected for instrumental resolution.

TABLE 3

THE MICROWAVE CONSTANTS OF CCH (in MHz)

MOLECULAR CONSTANT	THIS WORK[a]		SAYSTRY et al. 1981	ZIURYS et al. 1982
	Laboratory Data	Laboratory Plus Astronomical Data (recommended constants)		
B	43674.542 ± 0.008	43674.534 ± 0.006	43674.5135 ± 0.0054	43674.70 ± 0.10
D	0.1076 ± 0.0008	0.1071 ± 0.0008	0.1052 ± 0.0003	0.1137 ± 0.0006
$\nu_{10} = 2B - 4D$	87348.653 ± 0.016	87348.640 ± 0.012	87348.606 ± 0.011	87348.95 ± 0.20
γ	-62.647 ± 0.035	-62.606 ± 0.004	-62.661 ± 0.016	-62.62 ± 0.02
b	40.54 ± 0.20	40.426 ± 0.019	...	40.39 ± 0.14
c	12.26 ± 0.26	12.254 ± 0.026	...	12.32 ± 0.09

[a]Uncertainties are 1 σ derived from a least-squares fit.

data is in excellent agreement with that of HCN (Gottlieb *et al.* 1975).

The laboratory measurements confirm the astronomical identification of gaseous CCH by Tucker, Kutner, and Thaddeus (1974). With the recommended microwave constants in Table 3, CCH transition frequencies in the millimeter and submillimeter wave region can now be predicted to an accuracy of one part in 10^7 and Doppler velocities to an accuracy of 0.03 km s^{-1}. The uncertainty in b is 10 times smaller, and the uncertainties in γ and c 4 times smaller than in previously reported measurements.

V. DISCUSSION

Gaseous molecular ions and radicals have traditionally been difficult to observe in the microwave laboratory, but with recent improvements in instrumentation, particularly at high frequency, it is now evident that a fairly large number should be detectable. In addition to CCH, we have recently detected the even larger carbon chain radicals C_3N and C_4H (Gottlieb *et al.* 1982), which in the gas phase at least have previously been seen only in astronomical sources. A search is underway for other carbon chain radicals, as well as a systematic study of the isotopic species of CCH, starting with CCD because of the large fractionation of deuterium in some interstellar molecules.

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